

UNITED STATES PATENT APPLICATION

OF

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FOR

CEMENTED CARBIDE FOR OIL AND GAS APPLICATIONS
WITH TOUGHNESS FACTOR

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**CEMENTED CARBIDE FOR OIL AND GAS
APPLICATIONS WITH TOUGHNESS FACTOR**

This application claims priority under 35 U.S.C. §119 to Swedish Application No.
5 0203157-3 filed in Sweden on October 24, 2002; the entire contents of which is hereby
incorporated by reference.

FIELD OF THE INVENTION

The present invention relates to the new use of cemented carbide grade with special
10 properties for oil and gas applications. Moreover the invention refers to the application of a
corrosion and erosion-resistant grade including increased toughness characteristics for choke
valves to control the flow of multimedia fluid (gas, liquid and sand particles).

BACKGROUND OF THE INVENTION

15 Cemented carbide used for corrosion resistance in the demanding application of flow
control components within the oil and gas sector is subjected to a complex array of service
and environmental combinations. Moreover, the cost of "field" failures or unpredictable
service life is extremely high.

The opportunity to maintain or replace such equipment in the field, especially in
20 offshore deep-water sites, is limited by weather conditions. It is therefore essential that
reliable and predictable products form part of the subsea system.

US 6,086,650 discloses the use of an erosion resistant grade with submicron WC
grain size for severe conditions of multi-flow media, where these components suffer from
extreme mass loss by exposure to solid particle erosion, acidic corrosion, erosion-corrosion
25 synergy and cavitation mechanisms. Grades according to this patent have, however, turned

out to be unable to meet the conflicting demands of hardness (wear) and toughness, especially when the component design features require increased toughness levels.

SUMMARY OF THE INVENTION

5 It is therefore an object of the present invention to provide cemented carbide with good resistance to particle erosion under corrosion environment and improved toughness compared to prior art materials.

 This object has been achieved by using a specifically optimized multi alloy binder sintered with a submicron grain size WC and with a low carbon content.

10 According to a first aspect, the present invention provides a cemented carbide comprising, in weight %: 8-12% Co + Ni, with a Co/Ni weight ratio of 0.25 – 4; 1-2% Cr; 0.1-0.3% Mo; wherein essentially all of the WC grains have a size $< 1 \mu\text{m}$, and with a magnetic saturation cobalt content which is 80-90% of the chemically-determined cobalt content.

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DETAILED DESCRIPTION

 Cemented carbide with excellent properties for oil and gas applications regarding resistance to the combined erosion and corrosion synergistic effects at temperatures between -50 and 300°C, preferably 0-100°C, and toughness, according to the invention has the
20 following composition in weight %: 8 – 12% Co+Ni with a weight ratio Co/Ni of 0.25-4, 1-2% Cr and 0.1-0.3% Mo. Essentially all of the WC grains have a size $< 1 \mu\text{m}$.

 The hardness of the cemented carbide according to the invention shall be $> 1500 \text{ HV}_{30}$ (ISO3878), the toughness (K_{IC}) $> 11 \text{ MN/m}^{1.5}$ and the transverse rupture strength (TRS) according to ISO3327 $> 3200 \text{ N/mm}^2$.

In one preferred embodiment the cemented carbide has the composition in weight %:
3-4%, preferably 3.5%, Co, 6-8%, preferably 7%, Ni, 1-1.5%, preferably 1.3%, Cr and 0.2%
Mo. Balance is WC with an average grain size of 0.8 μm .

In another embodiment the composition is in weight %: 6-7%, preferably 6.6%, Co,
5 2-3%, preferably 2.2%, Ni, 1.0% Cr and 0.2% Mo. Balance is WC with an average grain size
of 0.8 μm .

The carbon content within the sintered cemented carbide must be kept within a
narrow band in order to retain a high resistance to corrosion and wear as well as toughness.
The carbon level of the sintered structure is held in the lower portion of the range between
10 free carbon in the microstructure (top limit) and eta-phase initiation (bottom limit).
Magnetic saturation measurements for the magnetic binder phase of the sintered cemented
carbide is expressed as a % of the maximum expected for that of the pure Cobalt content
contained in the carbide. For the sintered material according to the invention this should lie
between 80 and 90 % of the chemically determined content. No eta-phase is permitted in the
15 sintered structure.

Conventional powder metallurgical methods milling, pressing shaping and
sinterhipping manufacture the cemented carbide used in this invention.

The present invention also relates to the use of a cemented carbide according to
above particularly for the choke trim components used in the oil and gas industry where
20 components are subjected to high pressures of multi media fluid where there is a corrosive
environment, particularly for components, the primary function of which is to control the
pressure and flow of well products.

The principles of the present invention will now be further described by reference to
the following illustrative non-limiting examples.

Example 1

Cemented carbide grades with the following compositions in weight % were produced according to known methods and using WC powder with a grain size of 0.8 μm .

- A. WC, 3.5% Co, 7.0% Ni, 1.3% Cr, 0.2% Mo
- 5 B. WC, 6.6% Co, 2.2%, Ni, 1.0% Cr and 0.2% Mo
- C. WC and 6% Co
- D. WC and 6% Ni
- E. WC and 12% Co
- F. WC and 12% Ni
- 10 G. US 6,086,650 Example 1

The materials had the following properties

| Grade | Magnetic cobalt content, weight % | Average WC grain size, μm | Hardness HV30 | Toughness K_{IC} MN/mm ^{1.5} | TRS N/mm ² |
|--------------|-----------------------------------|--------------------------------------|---------------|--|-----------------------|
| A, invention | 2.7 | 0.8 | 1550 | 12 | 3300 |
| B, invention | 5.7 | 0.8 | 1650 | 11.2 | 4600 |
| C | 5.1 | 0.8 | 1700 | 10 | 2600 |
| D | 0 | 0.8 | 1700 | 9 | 2500 |
| E | 10.8 | 0.8 | 1400 | 12 | 3100 |
| F | 0 | 1.5 | 1400 | 11.5 | 3000 |
| G | 3.0 | 0.8 | 1900 | 9.1 | 2300 |

Example 2

- 15 The grades A-G were tested under the following simulated test conditions:

- Synthetic seawater

Sand 18 m/s

CO₂ 1 Bar

Temp. 54°C.

The following results were obtained.

Results

| Grade | Corrosion (material loss in mm/year) | Erosion (material loss in mm/year) | Synergistic (material loss in mm/year) | Total (material loss in mm/year) |
|--------------|--|--|--|--|
| A, invention | 0.01 | 0.05 | 0.05 | 0.11 |
| B, invention | 0.02 | 0.07 | 0.06 | 0.15 |
| C | 0.02 | 0.09 | 0.35 | 0.46 |
| D | 0.015 | 0.265 | 0.17 | 0.45 |
| E | 0.02 | 0.32 | 0.18 | 0.5 |
| F | 0.015 | 0.25 | 0.10 | 0.4 |
| G | 0.015 | 0.06 | 0.025 | 0.10 |

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Example 3

The grades were also tested under conditions of testing with flow loop containing sea-water and sand at 90 m/s flow rate at two impingement angles, 30 and 90 degrees with respect to the surface of test sample. The following results were obtained.

| Grade | Erosion rate (mm ³ /kg sand) | Erosion rate (mm ³ /kg sand) |
|--------------|--|--|
| Angle | 30 degrees | 90 degrees |
| A, invention | 0.47 | 0.32 |
| B, invention | 0.56 | 0.38 |
| C | 1.8 | 1.4 |
| D | 2.0 | 1.5 |
| E | 1.4 | 1.2 |
| F | 1.5 | 1.3 |
| G | 0.25 | 0.15 |

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